

# **POLAR TOLANE LIQUID CRYSTALS**

## **FIELD OF THE INVENTION**

The present invention relates to liquid crystal materials and eutectic mixtures thereof. In particular, the invention is directed to a new class of polar asymmetric tolane derivatives  
5 and eutectic liquid crystal mixtures containing the derivatives with infrared and microwave applications.

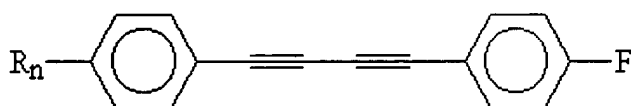
## **BACKGROUND OF THE INVENTION:**

Liquid crystals that have high birefringence, low viscosity, and low threshold voltage,  
10 and are capable of maintaining a nematic phase over a broad temperature range are desirable in electro-optic phase and amplitude modulation applications. Such applications include infrared light valves, polymer-dispersed liquid crystals and cholesteric displays. High birefringence, or optical anisotropy ( $\Delta n$ ), of the liquid crystal composition improves the efficiency of light modulation, and low rotational viscosity serves to shorten the  
15 response times. Low threshold voltage, which is inversely related to the dielectric anisotropy of the liquid crystal material, simplifies the electronics that drive the application.

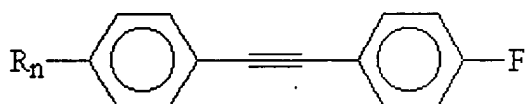
Polar liquid crystal compounds, particularly fluorinated species, have been investigated  
20 as possible candidates for such electro-optics applications. In general, fluorinated liquid crystal compounds have desirably low rotational viscosity, excellent photostability and

high resistivity. However, they also tend to exhibit modest dielectric anisotropy and, accordingly, high threshold voltage.

Increasing the asymmetry and, accordingly, the polarity of such compounds has been  
5 proposed as a means to improve the dielectric anisotropy of these compounds. Wu, et al. [Opt. Eng. 32, 1792-7 (1993)], for example, reported polar fluorinated diphenyldiacetylenes and tolans as shown in Structures I and II below, respectively



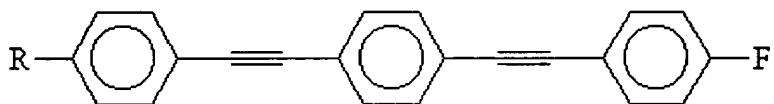
(Structure I)



(Structure II)

These compounds exhibit high birefringence, high resistivity, low viscosity, and comparatively low threshold voltage. However, while in some cases these compounds have reasonably low melting temperatures and heat fusion enthalpies, as is typical of  
15 compounds with high dipole moments, the melting temperature is too high and the nematic phase is too narrow.

The fluorination of polytolane liquid crystal compounds has also been investigated. In general, the highly conjugated polytolanes have desirably high birefringence. Fluorinated bis-tolanes such as shown in structure III, have been reported.

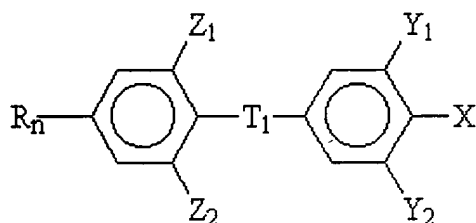


5 (Structure III)

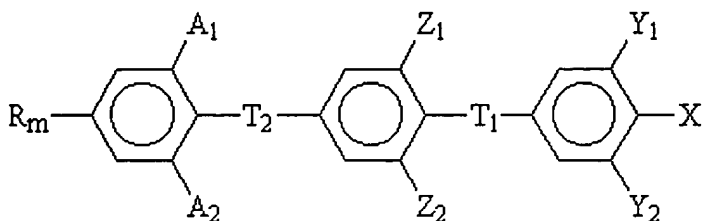
While this type of compound has good dielectric anisotropy, utility is limited, once again, due to high melting point and narrow nematic range.

### SUMMARY OF THE INVENTION

- 10 A new class of liquid crystal compounds is provided which provides improved melting points and broader nematic ranges compared to previously reported fluorinated liquid crystal compounds. Specifically, the present invention provides a class of compounds based on the tolane and bis-tolane structures as shown in Structures IV and V.



15 (Structure IV)

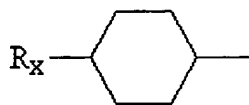


(Structure V)

- For the compounds depicted in all of the above structures and described herein, a polar group such as F (fluoro), CN (cyano), OCF<sub>3</sub> (trifluoromethoxy), or NCS (isothiocyanate) is positioned at site X and fluoro groups are positioned at least one of the pairs of sites Y<sub>1</sub> and Y<sub>2</sub>, Z<sub>1</sub> and Z<sub>2</sub>, and for the bis-tolane derivatives, A<sub>1</sub> and A<sub>2</sub>.

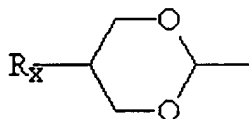
- For the tolane derivatives as depicted in structure IV, T<sub>1</sub> is always a triple bond. For the bis-tolane derivatives, T<sub>1</sub> and T<sub>2</sub> are either both triple bonds or one of the two groups is a double bond with and the other remains a triple bond.

- In this new class of compounds, R<sub>n</sub> or R<sub>m</sub> may be an alkyl group having the general formula C<sub>n</sub>H<sub>2n+1</sub>, an alkenyl group having the general formula C<sub>n</sub>H<sub>2n-1</sub>, an alkoxy group having the general formula OC<sub>n</sub>H<sub>2n+1</sub>, or an alkenoxy group having the general formula – OC<sub>n</sub>H<sub>2n-1</sub>. Additionally, for the tolane compounds depicted in structure IV, R<sub>n</sub> may be a cyclohexyl substituent as shown in Structure VI



(Structure VI)

or a dioxane substituent as shown in Structure VII.



(Structure VII)

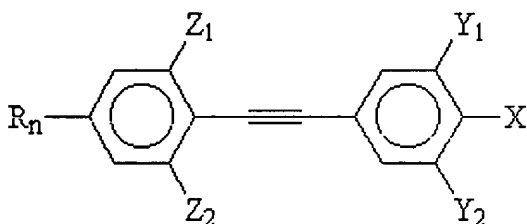
- 5 For both types of substituents,  $R_x$  may be an alkyl group having the general formula  
general formula  $-C_xH_{2x+1}$ , an alkenyl group having the general formula  $-C_xH_{2x-1}$ , an  
alkoxy group having the general formula  $-OC_xH_{2x+1}$ , or an alkenoxy group having the  
general formula  $-OC_xH_{2x-1}$ .

## 10 DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a new class of liquid crystal materials and eutectic  
mixtures thereof and a method for their synthesis. It is anticipated that the invention may  
be tailored to a variety of other applications. The following description is presented to  
enable one of ordinary skill in the art to make and use the invention and to incorporate it  
15 in the context of particular applications. Various modifications, as well as a variety of  
uses in different applications, will be readily apparent to those skilled in the art, and the  
general principles defined herein may be applied to a wide range of embodiments. Thus,  
the present invention is not intended to be limited to the embodiments presented, but is to  
be accorded the widest scope consistent with the principles and novel features disclosed  
20 herein.

The present invention relates, generally, to fluorinated polar asymmetric liquid crystal compound, a method for their preparation, and their use in eutectic mixtures. In certain embodiments of this invention, tolane compounds are provided of the type depicted in

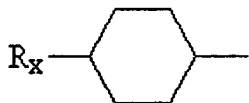
5 Structure VIII:



(Structure VIII)

wherein X is a polar group such as F (fluoro), CN (cyano),  $OCF_3$  (trifluoromethoxy), or NCS (isothiocyanate), and at least one of the pairs  $Y_1$  and  $Y_2$  and  $Z_1$  and  $Z_2$  are fluoro groups. In these embodiments,  $R_n$  may be an alkyl group having the general formula  $C_nH_{2n+1}$ , an alkenyl group having the general formula  $C_nH_{2n-1}$ , an alkoxy group having the general formula  $OC_nH_{2n+1}$ , or an alkenoxy group having the general formula  $OC_nH_{2n-1}$ . For these substituents, the value of n is preferably approximately 2 to 12.

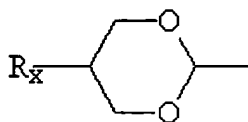
Additionally,  $R_n$  may be a substituent of the type shown in Structure VI,



(Structure VI)

wherein  $R_x$  is an alkyl group having the general formula  $C_xH_{2x+1}$ , an alkenyl group having the general formula  $C_xH_{2x-1}$ , an alkoxy group having the general formula

OC<sub>x</sub>H<sub>2x+1</sub>, or an alkenoxy group having the general formula OC<sub>x</sub>H<sub>2x-1</sub>. The value of x is preferably approximately 2 to 12. In yet another alternative, R<sub>n</sub> may be a substituent of the type shown in Structure VII,

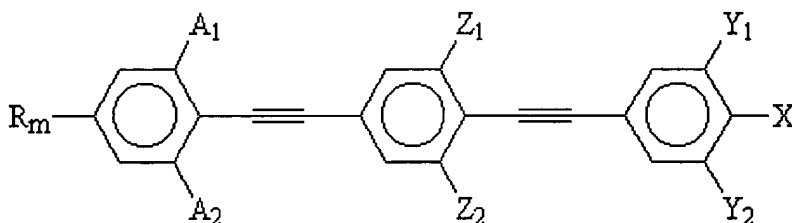


5 (Structure VII)

wherein again R<sub>x</sub> may be an alkyl group having the general formula C<sub>x</sub>H<sub>2x+1</sub>, an alkenyl group having the general formula C<sub>x</sub>H<sub>2x-1</sub>, an alkoxy group having the general formula OC<sub>x</sub>H<sub>2x+1</sub>, or an alkenoxy group having the general formula OC<sub>x</sub>H<sub>2x-1</sub>. Again, the value of x is preferably approximately 2 to 12.

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In other, preferred embodiments of this invention, bis-tolane compounds are provided as shown in structure IX,

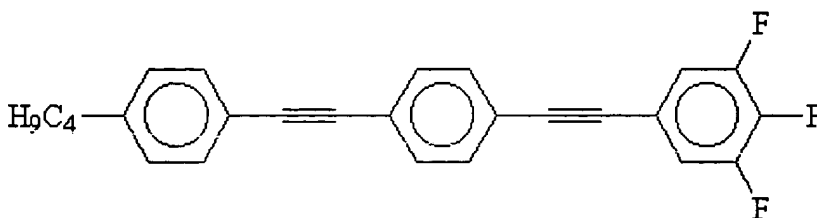


(Structure IX)

- 15 wherein X is a polar group such as F (fluoro), CN (cyano), OCF<sub>3</sub>(trifluoromethoxy), or NCS (isothiocyanate), and at least one of the pairs Y<sub>1</sub> and Y<sub>2</sub>, Z<sub>1</sub> and Z<sub>2</sub>, and A<sub>1</sub> and A<sub>2</sub> are fluoro groups. In this embodiment, R<sub>m</sub> may be an alkyl group having the general formula C<sub>m</sub>H<sub>2m+1</sub>, an alkenyl group having the general formula C<sub>m</sub>H<sub>2m-1</sub>, an alkoxy group

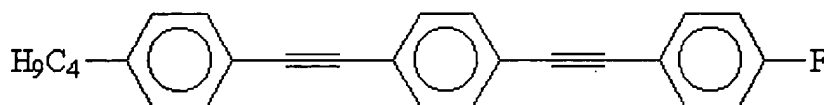
having the general formula  $\text{OC}_m\text{H}_{2m+1}$ , or an alkenoxy group having the general formula  $\text{OC}_m\text{H}_{2m-1}$ . The value of  $m$  is preferably approximately 2 to 12.

One example of this embodiment, wherein  $\text{R}_m$  is an alkyl group with  $m=4$ , is depicted  
5 for clarity in structure X and will henceforth be referred to as PTPTP-4FFF.



(Structure X)

This trifluoro bis-tolane compound has a nematic range of 115 to 188.1 °C and a heat  
fusion enthalpy of 3.85 kcal/mol. In comparison, the monofluoro compound, henceforth  
10 referred to as PTPTP-4F, and depicted in structure XI,



(Structure XI)

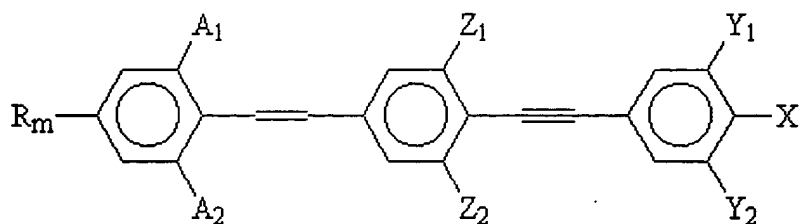
has a nematic range of 173.1 to 217.2 °C and a heat fusion enthalpy of 8.47 kcal/mol.

The addition of the fluoro groups meta to the tolane triple bond serves to reduce both the  
15 melting and clearing points of the compound and accordingly reduce the heat fusion  
enthalpy. Further, in contrast to PTPTP-4F, the reduced melting point of the PTPTP-  
4FFF species renders it useful in eutectic mixtures.

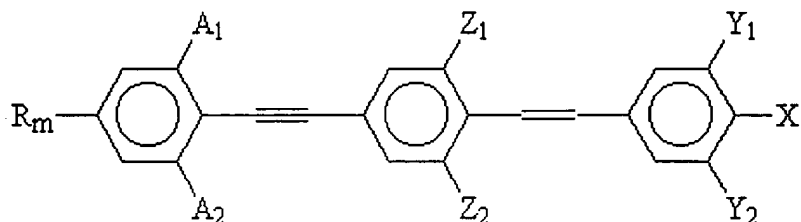


In yet other embodiments, modified bis-tolane structures of the types depicted in

Structures XII and XIII are provided:



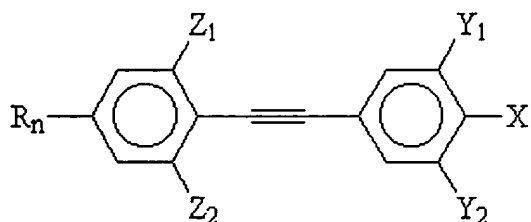
(Structure XII)



(Structure XIII)

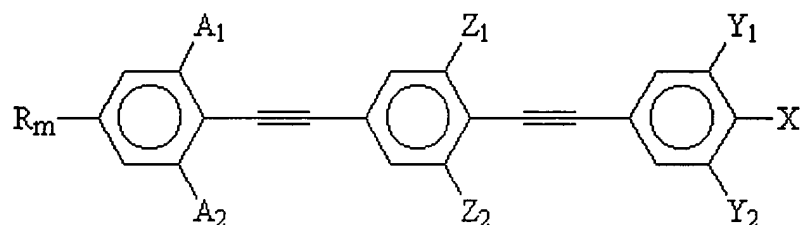
wherein X is a polar group such as F (fluoro), CN (cyano), OCF<sub>3</sub> (trifluoromethoxy), or NCS (isothiocyanate), and either the pair Y<sub>1</sub> and Y<sub>2</sub>, the pair Z<sub>1</sub> and Z<sub>2</sub>, or the pair A<sub>1</sub> and A<sub>2</sub> are fluoro groups and the alternate pairs are hydrogens. In this embodiment, R<sub>m</sub> may be an alkyl group having the general formula C<sub>m</sub>H<sub>2m+1</sub>, an alkenyl group having the general formula C<sub>m</sub>H<sub>2m-1</sub>, an alkoxy group having the general formula OC<sub>m</sub>H<sub>2m+1</sub>, or an alkenoxy group having the general formula OC<sub>m</sub>H<sub>2m-1</sub>. The value of m is preferably approximately 2 to 12.

For preferred embodiments of the tolans provided by the present invention as shown in structure VIII,

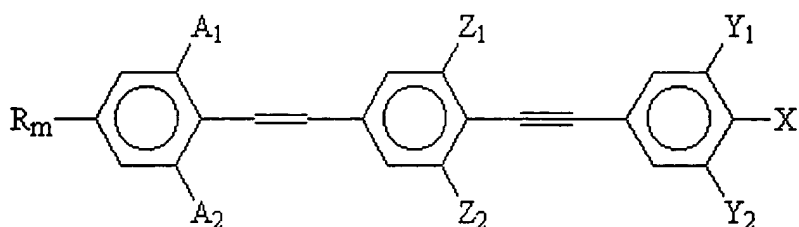


(Structure VIII)

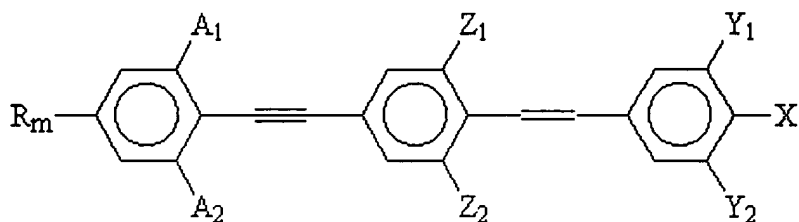
the  $R_n$  substituent is an alkenyl group having the general formula  $C_nH_{2n-1}$ , and more preferably an alkenyl group with the double bond in the second position and having the  
 5 general formula  $C_xH_{2x+1}CH=CH-CH_2-$ . Similarly for the bis-tolanes and modified bis-tolane derivatives shown structures IX, XII, and XIII,



(Structure IX)



10 (Structure XII)

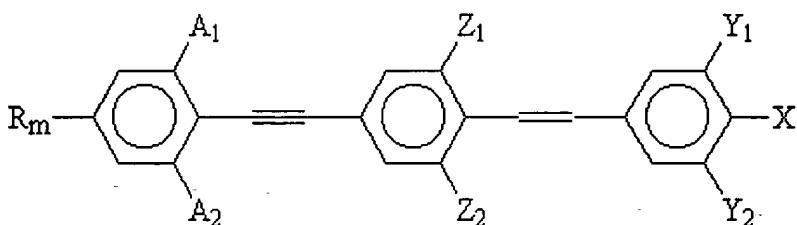


(Structure XIII)

$R_m$  is preferably an alkenyl group with the general formula  $C_mH_{2m-1}$ , and more preferably an alkenyl with the double bond in the second position and having the general formula

- 5  $C_xH_{2x+1}CH=CH-CH_2-$ . Furthermore, for the tolanes, bis-tolanes, and modified bis-tolanes provided herein, fluoro substitution at the X,  $Y_1$ , and  $Y_2$  positions is preferred.

Generally, the compounds provided in the present invention have large dipole moments that contribute to desirably high dielectric anisotropy. However, the positioning of the additional fluoro groups helps to reduce the high melting points characteristic of polar tolane and bis-tolane compounds. Modified bis-tolane structure XIII is shown here for reference.



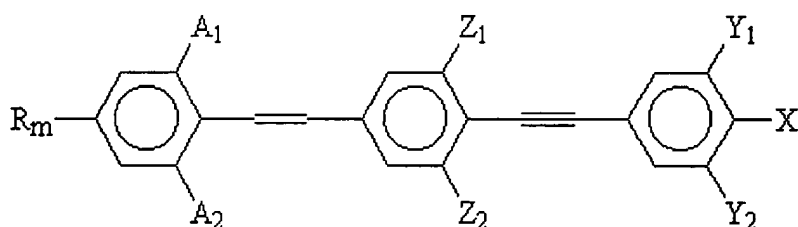
(Structure XIII)

- 15 However, the principles presented herein apply to all embodiments of the present invention. It should be apparent to one skilled in the art that placing fluoro groups in at

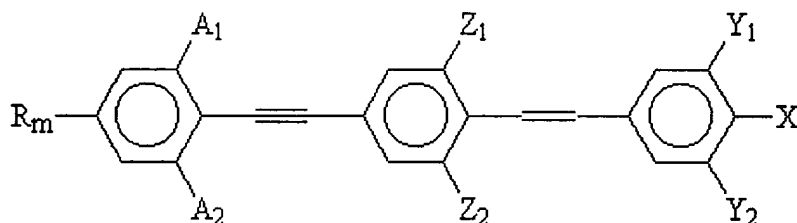
least one pair of the  $Y_1$ ,  $Y_2$ , or  $Z_1$ ,  $Z_2$ , or  $A_1$ ,  $A_2$  paired positions in the above structure not only contributes to the overall dipole of the molecule but also serves to increase the effective molecular distance between molecules in the bulk phase. Increasing the intermolecular distance results in a decrease in melting point and heat fusion enthalpy.

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For the modified bis-tolane embodiments of the present invention, reduction of one of the bis-tolane triple bonds to a double bond as shown in structures XII and XIII



(Structure XII)

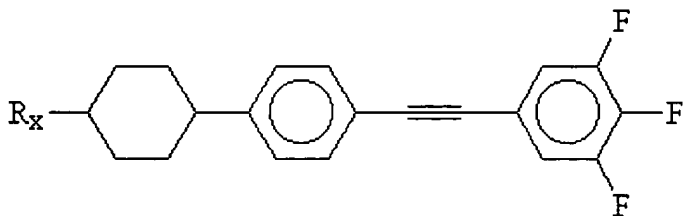


(Structure XIII)

introduces a bend into the molecular structure. This bend, like the pairs of fluoro substituents, serves to increase the intermolecular distance in the bulk phase. Thus, the reduction of one of the triple bonds in the bis-tolane structure results in a lower melting point and heat fusion enthalpy for the compound.

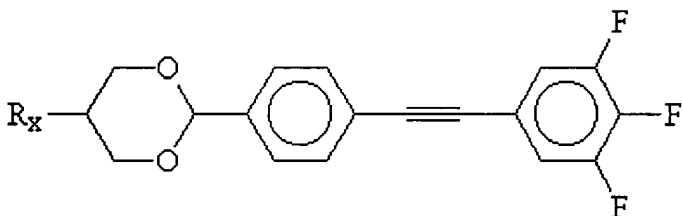
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In additional embodiments of the present invention, the compounds provided herein are utilized as components of eutectic mixtures. In general, compounds such as those depicted in structure XIV



5 (Structure IV)

are particularly effective due to low melting point and wide nematic range. Compounds such as PTPTP-4FFF and the class of compounds depicted in Structure XV,



(Structure XV)

10 while having relatively high melting points and limited nematic phases, are nonetheless useful as dopants for increasing the dielectric anisotropy of eutectic mixtures.

Compounds of the type shown in structure XV, in particular, have very high dipole moments and accordingly large dielectric anisotropy values.

15 General procedures for the preparation of embodiments of this invention are provided in Schemes 1 and 2. Scheme 1 outlines particularly the synthesis of the tolane compounds

(4), and Scheme 2 outlines particularly the bis-tolane variants (11). A detailed description of a synthesis example compound PTPTP-4FFF according to Scheme 2 is provided below. It will be readily apparent to one skilled in the art that the synthesis for PTPTP-4FFF described herein can be readily adapted, as outlined in Schemes 1 and 2, to produce other variants of the present invention. Appropriate selection of reactants, such as substituted benzenes, as outlined in the Schemes below will provide the desired products according to the present invention.

To a mixture of (trimethylsilyl)acetylene **1a** (5.0 g, 51 mmol) and 1-butyl-4-iodobenzene **5** (10.6 g, 46 mmol) was added the catalyst system of Pd(PPh<sub>3</sub>)Cl<sub>2</sub> (800 mg, 1.2 mmol) and CuI (220 mg, 1.2 mmol) followed by anhydrous tetrahydrofuran (50 mL). The mixture was kept under an Ar atmosphere and cooled with an ice-bath. Triethylamine (10 mL, 72 mmol) was added to the mixture through a syringe over 5 minutes and the orange solution was stirred for 1.5 hours while the ice-bath warmed up. The resulting dark solution was diluted with pentane and washed with 10% HCl, saturated NaHCO<sub>3</sub>, and brine, successively. The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub>, concentrated and passed through a plug of silica gel. Evaporation of solvent gave the trimethylsilyl acetylene derivative **6** as a clear oil (9.2 g, 100%).

To **6** (m = 4) (9.2 g, 46 mmol) was added a solution of NaOH (4 g, 100 mmol) in a mixed solvent of H<sub>2</sub>O (8 mL), THF (8 mL) and MeOH (8 mL). The mixture was stirred at room temperature for 17 hours. It was then diluted with hexanes and washed with 10% HCl, saturated NaHCO<sub>3</sub> and brine, successively. The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub>,

concentrated and passed through a plug of silica gel. Evaporation of solvent gave the unsubstituted acetylene compound **7** as a clear oil (5.5 g, 93%).

To an ice-bath-cooled mixture of **7** ( $m = 4$ ) (1.88 g, 11.9 mmol), 1-bromo-4-iodobenzene  
5 **7a** (3.06 g, 10.8 mmol),  $\text{Pd}(\text{PPh}_3)\text{Cl}_2$  (209 mg, 0.3 mmol) and  $\text{CuI}$  (57 mg, 0.3 mmol)  
were added tetrahydrofuran (12 mL) followed by triethylamine (5 mL). The mixture  
was stirred for 24 hours at room temperature. The precipitates were removed by vacuum  
filtration and the filtrate was diluted with pentane. The organic layer was washed with  
10% HCl, saturated  $\text{NaHCO}_3$  and brine, successively. After drying with  $\text{MgSO}_4$ ,  
10 concentration and filtration through silica gel, the brominated tolane **8** was obtained as a  
yellow solid (3.22 g, 95%).

To a solution of **8** ( $m = 4$ ) (743 mg, 2.4 mmol),  $\text{Pd}(\text{PPh}_3)\text{Cl}_2$  (28 mg, 0.01 mmol),  $\text{CuI}$  (5  
mg, 0.01 mmol) and  $\text{PPh}_3$  (10 mg, 0.01 mmol) in triethylamine (10 mL) was added  
15 (trimethylsilyl)acetylene (500  $\mu\text{L}$ , 3.6 mmol). The solution was refluxed under Ar for 1.5  
hours and then cooled to room temperature. Hexane extracts of the mixture were washed  
with 10% HCl, saturated  $\text{NaHCO}_3$ , and brine, successively. The solution was dried with  
 $\text{Na}_2\text{SO}_4$  and concentrated. The crude oil was subject to column chromatography to give a  
yellowish solid (604 mg, 84%) as the pure trimethylsilyl acetylene derivative **9**.

20 To a solution of **9** ( $m = 4$ ) (430 mg, 1.3 mmol) in the mixed solvent of tetrahydrofuran (6  
mL) and ethanol (6 mL) was added 1 g of Dowex® 550A  $\text{OH}^-$  anion-exchange resin.

The mixture was stirred at room temperature for 18 hours. After the resin was filtered, the solution was concentrated and filtered through silica gel (hexanes as eluent). Evaporation of solvent gave the unsubstituted acetylene derivative **10** as a yellow solid (350 mg, 100%).

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To a mixture of **10** ( $n = 4$ ) (182 mg, 1 mmol) and 1-bromo-3,4,5-trifluorobenzene **10a** (211 mg, 1 mmol) was added Pd(PPh<sub>3</sub>)<sub>4</sub> (12 mg, 0.01 mmol), CuI (2 mg, 0.01 mmol) and PPh<sub>3</sub> (4 mg, 0.01 mmol) followed by triethylamine (5 mL). The mixture was refluxed under Ar for 2 hours and cooled down to room temperature. It was then diluted with hexanes, filtered through silica gel and concentrated. Column chromatography of the crude oil gave the pure bis-tolane product **11** as a clear oil (80%).

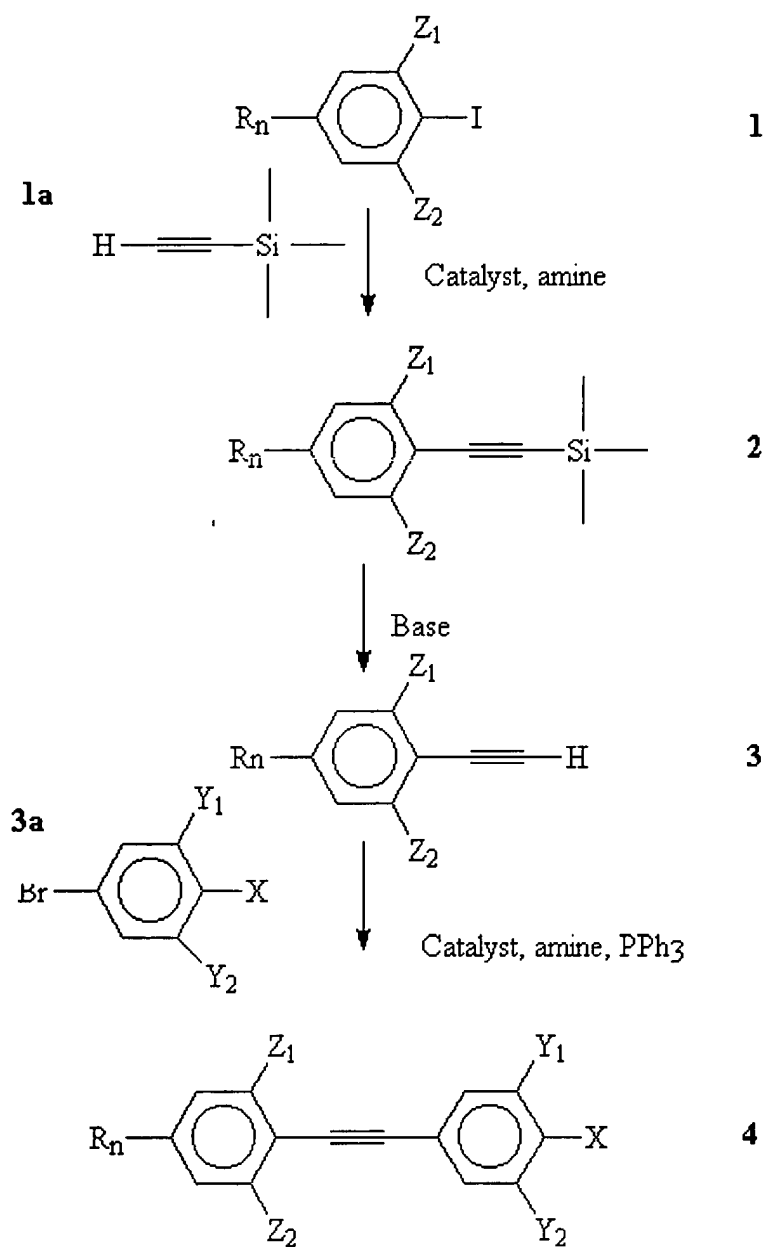
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Scheme 1



Scheme 2

